The influence of climate on in-stream removal of nitrogen

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[1] Nitrogen (N) removal via benthic denitrification in large river systems can be a significant sink of terrestrial N and a source of nitrous oxide (N_2O) to the atmosphere. Recent studies have demonstrated the fraction of in-stream N removed from a river reach is related to the water residence time. We used the HYDRA aquatic transport model to examine the sensitivity of in-stream N removal and the associated N_2O emissions in the Mississippi River system to the interannual variability in climate. The results suggested an almost two-fold range in the percent of N removed in the Mississippi River system and a three-fold range in the associated N_2O emissions, with the lowest percent removed (10–33%) and the highest N_2O emissions (15.5–26.0 10^6 kg N) occurring in the wettest years. The results demonstrate the importance of considering climate variability and change in the management of nutrient export by large rivers. *INDEX TERMS:* 1836 Hydrology: Hydrologic budget (1655); 1860 Hydrology: Runoff and streamflow; 1871 Hydrology: Surface water quality; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615). **Citation:** Donner, S. D., C. J. Kucharik, and M. Oppenheimer (2004), The influence of climate on in-stream removal of nitrogen, *Geophys. Res. Lett.*, *31*, L20509, doi:10.1029/2004GL020477.

1. Introduction

[2] The mobilization of N by agricultural and industrial activity has increased N export by rivers worldwide [*Galloway et al.*, 2003]. An emerging body of research is dedicated to understanding the fate of natural and anthropogenic N in large river basins [*Seitzinger and Kroeze*, 1998; *Alexander et al.*, 2000; *Donner et al.*, 2004]. A key uncertainty is the removal of N during transport through the river system.

[3] The most significant removal process is denitrification in the sediments, in which nitrate (NO_3) is reduced to di-nitrogen gas (N_2) and the greenhouse gas nitrous oxide (N_2O). Denitrification is a difficult process to represent in large-scale models, as it occurs in small anaerobic pockets in the soil and depends on the NO_3 availability, carbon (C) availability, temperature and substrate composition. Recent studies have found the percent of NO_3 (or total N) removed via denitrification tends to vary across a river network with the water residence time [*Howarth et al.*, 1996; *Alexander et al.*, 2000; *Seitzinger et al.*, 2002]. Several models based upon hydrologic properties suggest that the fraction of river N removed is greatest in low-flow or headwater streams due to more frequent contact with between river N and the sediments [*Alexander et al.*, 2000; *Seitzinger et al.*, 2002]. This relationship implies that the in-stream removal fraction could also be lower during wet periods, when there is less frequent contact between river water and the sediments.

[4] In this study, we examine how interannual variability in climate and river hydrology influences in-stream NO_3 removal and associated N_2O emissions, using a model of N, water and C cycling in the Mississippi River Basin [*Donner et al.*, 2004]. The percent of NO_3 loading removed during transport may be lower in wet years, contributing to even higher NO_3 export. This would complicate efforts to manage nutrient export by rivers like the Mississippi in the face of climate variability and future climate change.

2. Model Description

[5] We simulate NO_3 flux, in-stream NO_3 removal and river discharge in the Mississippi River system from 1960–94 with the HYDRA hydrological transport model. HYDRA simulates the time-varying flow and storage of water and N in rivers, wetlands, lakes and reservoirs at $5' \times 5'$ spatial resolution at an hourly time step based upon upstream inputs, local surface runoff, subsurface drainage and N leaching, precipitation and evaporation over surface water, and topography [*Coe*, 1998; *Donner et al.*, 2002]. The model simulates the movement of NO_3 since it comprises the majority of dissolved inorganic N loading in the Mississippi Basin [*Goolsby and Battaglin*, 2001].

[6] The inputs of surface runoff, sub-surface drainage and NO_3 leaching to the river system are derived from previous simulations with IBIS, a dynamic land surface model. IBIS describes the movement of water, C and N through vegetation and soils in both natural and agricultural ecosystems over time based upon physical, physiological and biogeochemical principles [*Kucharik et al.*, 2000]. IBIS and HYDRA have been extensively tested and applied towards understanding hydrology and biogeochemical cycling across the Mississippi Basin [e.g., *Donner and Kucharik*, 2003]. In *Donner et al.* [2004], IBIS accurately recreated the trend and interannual variability in the water and N budget of the Mississippi Basin since 1960 using historical datasets of climate, land cover, atmospheric N-deposition and N-fertilizer application rates. We use the monthly IBIS output for 1960–1994 from that simulation as input to HYDRA; for a review of the input data and model validation, see *Donner et al.* [2004].

[7] HYDRA assumes that denitrification in the aquatic sediments is the only permanent N removal process. Although river N does cycle between the water column, biota and sediments, it eventually either travels downstream

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Table 1. Simulated Annual In-Stream Removal (1960–1994)

HYDRA Simulation	In-Stream Removal, %	
	Median	Annual Range
1. *Donner et al.* [2004]	24	18–33
2. No temp variation[a]	24	18–32
3. Sinuosity = 1.4	30	23–40
4. K −50%	14	10–20
5. K +50%	31	24–42
6. K ↓ with discharge[b]	32	26–43
7. Combination (2, 3, 6)	41	33–50

[a]Q10 relationship replaced with average value (2.534).
[b]$K = 0.06 - (0.0075) \times \log(Q)$; max of 0.6, min of 0.2.

or is reduced to N_2 or N_2O by denitrifying bacteria [*Peterson et al.*, 2001]. The NO_3 removal in each grid cell (L, kg s^{-1}) is calculated at each time step from the river bed area (A_b, m^2), water temperature (T, °C), NO_3 concentration (C_N, kg m^{-3}) and a rate parameter (K, m s^{-1}):

$$L\left(\text{kg s}^{-1}\right) = K \times 10^{0.0293\,T} \times A_b \times C_N$$

[8] This function describes the rate at which NO_3 contacts the sediments (A_b, C_N) and whether that NO_3 is denitrified (K, T). A_b is determined from river length and the river width, using a discharge-based rating curve; C_N is determined from the water volume and NO_3 mass in the river reach. In previous studies, K was set at 0.04 m day^{-1}, based on existing models [*Howarth et al.*, 1996] and calibration with observed microbial denitrification rates [*Donner et al.*, 2002]. An adjustment ($\times 120\ m^3 s^{-1}/Q$) was applied above a discharge threshold to reflect the low removal rates in high order rivers [*Goolsby and Battaglin*, 2001]; it has a negligible effect on total in-stream removal from the river network.

[9] Previous research found that HYDRA, with inputs of runoff, drainage and NO_3 from IBIS, captured the relationship between NO_3 removal and water residence time noted in other studies, the expected seasonal variation in NO_3 removal and the range of observed microbial denitrification rates [*Donner et al.*, 2002, 2004]. The mean fraction of NO_3 loading removed via denitrification was lower than estimates of total N removal from large river systems by the empirical models SPARROW [*Alexander et al.*, 2000] and Riv-N [*Seitzinger et al.*, 2002]. A direct comparison of HYDRA and such steady-state models is difficult, because of the short time step in HYDRA. But the central logic is consistent across models (Appendix A).

3. Description of Simulations

[10] We tested fifteen different variations on the initial denitrification function to estimate how annual in-stream N removal in the Mississippi River system and associated N_2O emissions respond to climate. The sensitivity tests were conducted to determine the robustness of the relationship between in-stream removal and climate. The tests included combinations of altering K (e.g., ±50%, decrease with increasing Q), introducing a term for river sinuosity to better represent the travel time and bed area [*Costa et al.*, 2002] and changing the temperature dependence. A control simulation, without in-stream removal, represents the total NO_3 loading from IBIS to the river system in HYDRA. The fraction of NO_3 loading removed via denitrification (referred to as the removal fraction, using unit-less points to avoid confusion) is calculated from the difference between each simulation and the control. Results from seven representative simulations (Sim 1–7) are presented.

4. In-Stream NO_3 Removal

[11] The annual mean in-stream NO_3 removal in the sensitivity simulations ranges from 14–41% of the total loading to the river system (Table 1). The interannual variability in the removal fraction is similar ($r^2 > 0.76$) in each the simulations, revealing an underlying sensitivity to climate (Figure 1). The annual removal fraction varies almost two-fold by 10–18 points in each simulation (e.g., 23–40% in Sim 3) with lowest values during high rainfall, high runoff years, like 1993, and highest values during low rainfall, low runoff years like 1977. During wet years, greater runoff and soil-N loss lead to high NO_3 loading to the river system; but greater river discharge decreases the likelihood the average river NO_3 molecule will contact the sediments and undergo denitrification. The simulations suggest the observed 25% increase in Mississippi River discharge from the 1960s to 1990s may therefore have caused a 3–5 point decrease in the removal fraction.

[12] It is difficult to validate the simulated in-stream removal without high-resolution observations of NO_3 loading from land over time or an extensive network of denitrification field data. The simulated response of both river discharge and NO_3 flux to climate variability does provide confidence in the simulated interannual variability in the removal fraction. Annual river discharge is strongly correlated with USGS observations at the mouth of the Mississippi and the eight major sub-basins ($r^2 > 0.67$). There is also strong agreement ($r^2 > 0.83$) between the annual NO_3 flux in each simulation and USGS observations for the Mississippi River at St. Francisville, LA, the station closest to the mouth with long-term records (Figure 2). The strong correlation is not surprising, since IBIS reproduces the expected interannual variability in NO_3 loading to the river system [*Donner et al.*, 2004] and the interannual variability in the removal fraction is similar in each of the HYDRA simulations. Even if there is some error in the mean NO_3 loading from IBIS, the simulations still

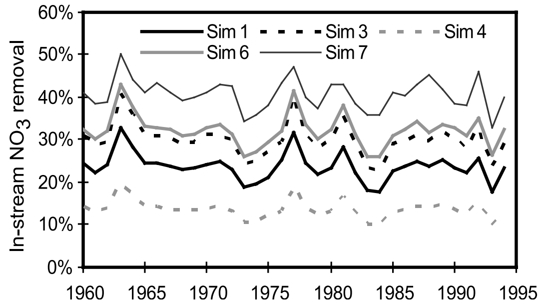

Figure 1. Annual in-stream removal (%) in the Mississippi River Basin (1960–1994) from selected simulations. A representative range of the seven simulations are displayed for presentation purposes.

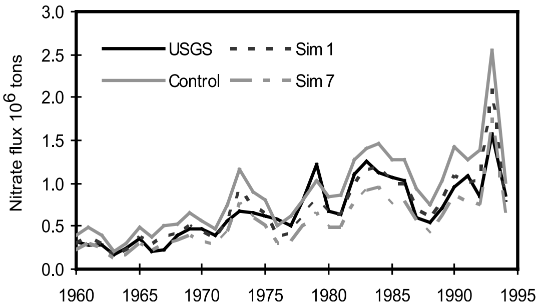

Figure 2. Simulated and observed annual NO3 export (ton yr-1) by the Mississippi River at St. Francisville, Louisiana for the 1960–1994 period. Only the control (no denitrification) simulation, representing total nitrate inputs to the river system, and two of the seven sensitivity simulations are displayed for presentation purposes.

Table 2. Annual In-Stream Removal (1960–1994), Sim 3

	In-Stream Removal, %		
Watershed	Median	Annual Range	Runoff, m yr^{-1}
Tennessee	20	14–30	0.67
Allegheny	21	16–26	0.56
Iowa	31	21–47	0.47
Muskinghum	26	20–33	0.38
Illinois	26	19–43	0.36
Rock	25	17–50	0.35
Grand	32	19–50	0.29
Canadian	65	45–78	0.06
Yellowstone	55	40–74	0.03

provide plausible representation of the response of in-stream removal to climate.

[13] The sensitivity tests demonstrate that representing river sinuosity, the rate parameter K and the temperature effect is crucial to describing the mean in-stream removal, but has less impact on the interannual variability. The introduction of river sinuosity (e.g., Sim 3) to HYDRA increases the simulated bed area in each grid cell and thereby the magnitude of NO_3 removed. A dataset of river sinuosity and other flow parameters [e.g., *Costa et al.*, 2002] would improve simulation of nutrient cycling in large river basins.

[14] Assuming an accurate representation of the bed area, the key uncertainty is the rate at which NO_3 that contacts the sediments is denitrified, represented here by K and the Q10 temperature relationship. With the initial value of K (0.04 m day^{-1}) and a mean Q10 value, the rate is 37 m yr^{-1}, similar to the 35 m yr^{-1} mean uptake rate used by *Howarth et al.* [1996]. More recent models like Riv-N describe an exponential increase in the removal fraction the water residence time in a river reach; that would suggest K should decrease with discharge as in Sim 6 and 7. The results of Sim 7 are within the range predicted by SPARROW for the Mississippi, although that model describes total N removal which may include sedimentation behind dams.

[15] Removing the temperature dependence (Sim 2) from HYDRA has a negligible impact on the interannual variability in the removal fraction, apart from a small change (<5 points) in anomalously warm or cold years. A climate-induced increase in water temperatures over time could increase denitrifier activity but is unlikely to be the primary factor influencing basin-wide in-stream removal. Other factors, like nitrate and carbon availability, are often more limiting than temperature [*Seitzinger*, 1988].

[16] The sensitivity of simulated in-stream removal to variability in hydrology and climate depends largely on the characteristics of the watershed. The annual mean removal fraction varies three-fold across a selection of diverse sub-basins of the Mississippi river system (Table 2). The removal fraction is higher and more variable in drier watersheds with more meandering rivers (e.g., Canadian, Yellowstone) than wetter watersheds (e.g., Tennessee, Allegheny). The coefficient of variation (CV) of annual removal fraction is highest the watersheds with the highest CV of runoff (Table 2).

[17] The results suggest a similar statistically significant decrease in the removal fraction with increasing precipitation or runoff (Figure 3). In the dry, low relief Yellowstone basin, the simulations suggest a 200 mm increase in precipitation would reduce the removal fraction by 12–16 points. But in the more humid Allegheny, the same precipitation increase translates to a negligible 0–2 point drop. The removal fraction for the entire Mississippi river system is moderately sensitive to precipitation - varying 4–7 points with a 200 mm change - since it integrates the response of the many sub-basins.

5. N_2O Emissions

[18] Only a small fraction of the NO_3 that undergoes denitrification is released to the atmosphere as N_2O. The N_2O:N_2 emission factor (EF) from denitrification in aquatic sediments can vary with pH and NO_3, C and oxygen availability [*Seitzinger*, 1988; *Groffman et al.*, 2000]. The EF may increase above a threshold NO_3 concentration, because the N_2O produced by denitrification is less likely to be reduced to N_2 when excess NO_3 is also available as an electron acceptor [*Groffman et al.*, 2000]. In estimating global N_2O emissions from rivers, *Seitzinger and Kroeze* [1998] assigned an EF of 0.003 (0.3%) where the N loading is below 10 kg N ha^{-1} and an EF of 0.03 (3%) above the threshold, based on field observations.

[19] We adapted this formulation for HYDRA to estimate the variability in N_2O emissions from benthic denitrification in the Mississippi Basin. The loading threshold was con-

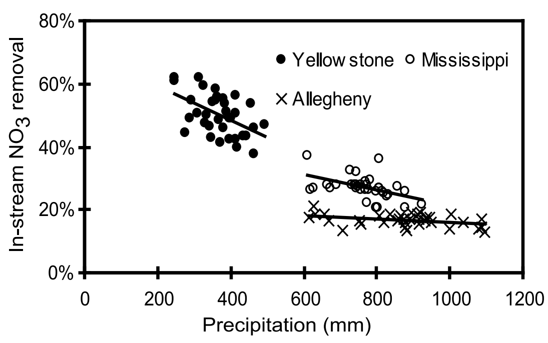

Figure 3. Annual in-stream removal (%) vs. annual precipitation (mm) for two sub-basins and the entire Mississippi Basin in Sim 3.

Table 3. Simulated N_2O Emissions From Benthic Denitrification in the Mississippi Basin (1980–1994)

Experiment	Emissions, 10^6 kg N	
	Median	Annual Range
1. *Donner et al.* [2004]	9.3	5.4–15.5
3. Sinuosity = 1.4	11.5	6.54–22.1
6. K ↓ with discharge	11.4	6.53–19.9
7. Combination	15.0	8.65–26.0
Seitzinger and Kroeze	2.1	n/a

verted to an equivalent river NO_3 concentration (3 mg L^{-1}) via regression of simulated loading and concentrations in 25 small watersheds. Total annual N_2O emissions were estimated from monthly NO_3 removal in each grid cell for 1980–94, when N inputs to the landscape were relatively constant.

[20] The simulated mean annual N_2O emissions from denitrification ranges from 9.3 to 15.0 million kg N in the seven simulations, four to eight times greater than the *Seitzinger and Kroeze* [1998] estimate (Table 3). The difference is not surprising; *Seitzinger and Kroeze* [1998] underestimated N loading in the Mississippi Basin by almost 50%, while IBIS overestimated N loading to river system in the western parts of the Mississippi Basin [*Donner et al.*, 2004]. Assuming the EF formulation is a reasonable representation of reality, the actual emissions should be at the lower end of the range in this study.

[21] In each simulation, there is a threefold range in annual N_2O emissions with the highest emissions occurring in the wettest years. Although the removal fraction is lowest in wet years, the total mass of NO_3 removed - and the N_2O emissions - is higher because of the greater NO_3 loading from land. Validating the magnitude of these simulated emissions is difficult since they represent a small fraction of total N inputs to the landscape (<0.1% in this study). The large interannual variability shows that closing the global N_2O budget will require accurate estimates of N loading from land and modeling of river N cycling over multiple years.

6. Discussion

[22] This study shows that the fraction of river N removed via denitrification across a large river basin should be significantly lower during wet years due to less frequent contact between stream N and the sediments. The relationship between in-stream removal and hydrology is consistent with the logic of other river N models [e.g., *Alexander et al.*, 2000]. It is possible the model underestimates removal during the wettest years by not explicitly representing the engagement of shallow floodplains or the influence of greater C delivery on denitrifier activity. Without the wettest years, the simulations still predict a 12–14 point range in the removal fraction and two-fold range in the N_2O emissions.

[23] A comprehensive assessment of in-stream N cycling and the associated N_2O emissions must include dynamic simulation of hydrology. It is particularly crucial in heavily fertilized river basins like the Mississippi where a small increase in rainfall can lead to a large increase in N loading to the river system [*Donner and Kucharik*, 2003]. These results show that during a wet year, not only does N loading from land increase, the fraction of N removed before reaching the ocean decreases. Higher runoff could reduce the efficacy of mitigation practices designed to increase N removal from the river system.

[24] The increase in precipitation and river discharge in the Mississippi River Basin since the 1960s has already influenced N cycling, contributing to as much as a quarter of the observed increase in NO_3 export to the Gulf [*Donner et al.*, 2002]. Acceleration of the hydrologic cycle in a warmer climate may lead to a further increase in the frequency of high runoff years in river basins like the Mississippi [*Milly et al.*, 2002]. The historical precedent and future projections further demonstrate the need to consider climate variability and climate change in water quality policy and estimates of the N_2O budget.

Appendix A: Model Comparison

[25] The in-stream removal fraction (R, %) at a given time step can be expressed as the ratio of the loss rate (L, kg s^{-1}) and the NO_3 flux (kg s^{-1}), a product of the concentration (C_N) and river discharge (Q):

$$R = L/(C_N \times Q) = \left(K \times 10^{0.0293T} \times A_b\right)/Q$$

[26] Removal decreases with increasing Q, because A_b:Q decreases. Models like Riv-N [*Seitzinger et al.*, 2002] state that R increases with water residence time or as the ratio of depth (D, in m) to travel time (T) decreases. In an idealized river reach,

$$D:T = (\mathrm{Volume}/A_b) : (\mathrm{Volume}/Q) = Q : A_b$$

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